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Invention Manufacturing Process of Polymer Electrolyte Fuel Cell

Abstract

[Objective] This invention aims at providing high performance polymer electrolyte fuel cell (PEFC) without conventional polytetrachloroethylene using remarkably simplified manufacturing process.

[Content] The invented method consists of (1) forming a slurry by mixing a electrocatalyst of platinum supported carbon black, a solution of ion-exchange resin used as polymer electrolyte and diluent, (2) coating the slurry as a film on electrodes which is subjected to water repel treatment, (3) making electrode sheets by evaporating the solvent in the slurry, (4) sandwiching the polymer electrolyte between these two electrode sheets and then (5) joining the electrodes and the polymer electrolyte as one body with hot pressing.

Scope of the patent application

[Application 1] Manufacturing process of PEFC based on joining both electrodes and electrolyte (ion-exchange resin) with hot pressing. The process is as follows. (1) Forming a slurry by mixing a electrocatalyst of platinum supported carbon black, a solution of ion-exchange resin used as polymer electrolyte and diluent, (2) coating the slurry as a film on electrodes which is subjected to water repel treatment, (3) making electrode sheets by evaporating the solvent in the slurry, (4) sandwiching the polymer electrolyte between these two electrode sheets and then (5) joining the electrodes and the polymer electrolyte as one body with hot pressing.

[Application 2] Above mentioned manufacturing process in the case that weight of the solvent solution of the ion-exchange resin (electrolyte solution) is in the range of 5–50 (as a resin) per electrocatalyst weight of 100, weight of the diluent is in the range of 100–400 per electrolyte solution weight of 100 and the solid concentration in the slurry is in the range of 2.5–25 wt%.

[Application 3] Above mentioned manufacturing process in the case that the amount of the slurry applied on the electrodes is in the range of 0.01-4 mg / cm^2 (as platinum content).

Detailed explanation of the invention

[0001]

[Applicable field in industry] This invention is related to manufacturing process of polymer electrolyte fuel cell.

[0002]

[Conventional technology and problem] So far, as a fabrication method of PEFC, the following process is known. At first, electrode sheets are produced by mixing electrocatalyst particles prepared in advance and PTFE (Polytetrafluoroethylene), and then these electrodes are bonded to the ion-exchange resin with thermo-compression bonding (For example, US patent 3134697, 3297484 and 3432355). However, this method is not satisfactory because the thermo-compression bonding between the electrodes and the electrolyte can not be done simultaneously with binding of electrodes due to high binding temperature of the electrodes. Therefore, the fuel cell performance is not so good.

[0003] Another fabrication method of PEFC that the catalyst particles are deposited in the ion-exchange resin (near the surface of the resin) with chemical reduction is reported (For example, Japanese patent 58-47471). However, this process has a shortcoming that the catalyst tends to exist as particles, in other words, the catalyst highly disperses, therefore it is very difficult to maintain electrical contacts.

[0004] In Electrochemistry 53 (No. 10, 1985, p812-817), the bonding method of oxygen electrode is shown. 10 % platinum supported carbon powder is used as electrocatalyst of

the oxygen electrode. Mixed solvent solution consisted of Nafion-117 (perfluorocarbon-sulfonic acid resin, DuPont, trade name) solution (aliphatic alcohol containing 5 % Nafion-117) and water are added to the electrocatalyst powder with various ratio, and then 60 % of PTFE aqueous suspensions are added. After the resulting mixtures are kneading, oxygen electrode sheets are produced by rolling and vacuum drying, and then the oxygen electrodes are hot-pressed to Nafion-membrane (DuPont, polymer electrolyte, trade name) at a temperature of 100 °C with 210 kg / cm^2. It is repotted that according to this method, the mixing of the ion-exchange resin into the oxygen electrode bonded with polymer electrolyte results in three dimensional electrochemical reaction sites which lead to notable improvement of polarization property. However, performance of the PEFC fabricated by the above mentioned method is not sufficient due to the use of PTFE. Moreover, the manufacturing process is complicated because of kneading and rolling processes.

[0005] In Japanese Patent 4-162365, the following process for fabricating fuel cell electrode is shown, 30 wt% platinum supported carbon black is immersed in butanol solution (Solute: Nafion) and then the catalyst particles coated with Nafion can be obtained by drying under vacuum. Another batch of carbon black without electrocatalyst is immersed in the butanol solution (Solute: Nafion), and then the no-catalyst particles coated with Nafion are obtained. Next, the mixture of these two particles (with and without catalyst) are mixed with PTFE dispersion, and then the mixture is filtrated and dried. The resulting powder mixture is normally used as basis of the fuel cell electrode. The powder mixture is spread on the carbon paper which is subjected to water repel treatment with 20 wt% PTFE so that the amount of platinum becomes 0.5 mg / cm^2, and then the electrodes are formed by pressing the coated carbon paper at 130 °C with 40 kg / cm^2 for 5 seconds. The ion-exchange resin (Nafion-117) is sandwiched between the two electrodes, afterwards the layer is pressed to one body at 160°C under the pressure of 40 kg / cm^2 for 5 seconds. It is reported that using this process, high performance and low cost electrodes can be obtained with small amount of catalyst, therefore manufacturing of portable-high powder density fuel cell is possible. However, above mentioned technique has disadvantage of significantly complicated process, furthermore has a problem of electrode formation due to no heat-treatment above 360°C (PTFE binding temperature).

[0006] This invention aims at providing high performance polymer electrolyte fuel cell (PEFC) without conventional polytetrachloroethylene using remarkably simplified manufacturing process.

[0007]

[The way to solve the problems] This invention provides the PEFC fabricated by the following technique. At first, a slurry is formed by mixing an electrocatalyst of platinum supported carbon black, a solution of ion-exchange resin used as polymer electrolyte and diluent. Next, the slurry is coated as a film on the electrodes which are subjected to water repel treatment. And then, the electrode sheets are established by evaporating the solvent in the slurry. A polymer electrolyte is sandwiched between these two electrode sheets and then the electrodes and the polymer electrolyte assembly are joined as one body with hot pressing.

[0008] In this invention, the amount of platinum added to carbon black is normally in the range of 5-40 wt%, preferably in the range of 25-40 wt%.

[0009] Nafion-117 is given as an example of the ion-exchange resin as polymer electrolyte in this invention. Mixed solvent solution consisted of alcohol solution of Nafion-117, aliphatic alcohol and water is given as a solvent solution of the ion-exchange resin. The concentration of the resin is normally in the range of 0.1-5 wt%, preferably in the range of 1-5 wt%.

[0010] The diluent in this invention is used for uniformizing the slurry. Solvent mixtures of aliphatic acids and water, preferably the mixture of i-propanol and water or the mixture of n-butanol and water are given as examples.

[0011] In this invention, there is no restriction on the order of mixing processes. Simultaneous mixing of the platinum supported catalyst, the solvent solution of ion-exchange resin and the diluent is also acceptable. It is preferable to mix uniformly with a ultrasonic homogenizer. By this mixing the slurry can be obtained.

[0012] In this invention, concerning the mixing ratio of the platinum supported catalyst, the solvent solution of ion-exchange resin and the diluent, weight of the solution of ion-exchange resin (electrolyte solution) is in the range of 5-50 (as a resin) per catalyst weight of 100, preferably in the range of 10-50, and weight of the diluent is in the range of 100-400 per electrolyte solution weight of 100, preferably in the range of 200-400. If

the weight of the resin is less than 5 per catalyst weight of 100, the resin does not spread sufficiently in the catalyst particles. In contrast, if the weight exceeds 50 per catalyst weight of 100, some parts of ion-exchange resin have no electrocatalyst. These situations are not desirable in terms of the film formation. If the weight of the diluent is less than 100 per the weight of the electrolyte solution of 100, it is difficult to obtain uniform slurry. In contrast, if the weight of the diluent exceeds 400, evaporation process of the solvent takes long time. These situations are also not desirable. Moreover, the amount of the diluent is defined as the weight giving the solid concentration of 2.5-25 wt%, preferably 5-25 wt% in the formed slurry. The concentration less than 2.5 wt% is not preferable due to long time evaporation of the solvent, and the concentration more than 5 wt% is also not preferable due to difficulty of getting uniform slurry.

[0013] The slurry formed by the above mentioned technique is constructed as a film on the electrode basis subjected to water repel treatment. In this case, the amount of the slurry corresponds to 0.01-4 mg / cm^2 of platinum amount. If the amount of platinum is less than 0.01 mg/ cm^2, the number of active sites are too small and reasonable current can not be generated. To the contrary, if the amount becomes more than 4 mg / cm^2, reaction layer becomes thicker. This results in higher polarization. Carbon papers are well-known as a electrode basis. The papers with the porosity of 50-90 % can be used, however these papers with the porosity of 70-80 % are preferable. As for the water repel treatment of the electrode basis, the well-known process using PTFE can be adopted. The well-known various painting methods, printing methods and doctor-blade methods can be applied to fabricate the catalyst film on the electrode basis.

[0014] Consequently, the electrode sheets can be produced by evaporating the solvent in the coated slurry. The evaporation of the solvent can be performed at 80°C with vacuum drying.

[0015] Next, the ion-exchange resin as an electrolyte is put between the two electrode sheets, and then the assembly is hot-pressed to one body. The hot-pressing is carried out at the temperature range of 140-200°C under the pressure of 25-200 kgf / cm^2 for 3-180 seconds.

[0016] The conventional current collectors are attached to both surfaces of the resulting assembly. The PEFC can be constructed by setting up gateways of oxygen and hydrogen in this assembly.

[0017]

[The effect of the invention] This invention provides high performance PEFC, especially can generate large current at relatively low operating temperature without conventional polytetrachloroethylene using remarkably simplified manufacturing process.

[0018]

[Practical example] In the following section, this invention will be described in detail, through the practical example.

[0019] Practical example 1

The mixture consisted of 100 g of 40 wt% platinum supported carbon black, 800 g of alcohol solution containing 5 wt% Nafion-117 and 1600 g of water-alcohol (1:4) solvent was mixed uniformly using ultrasonic homogenizer. And the slurry with the solid concentration of 5.8 wt% was formed. The slurry was painted uniformly on the carbon paper (75 % in porosity, 0.4 mm in thickness, subjected to water repel treatment using 25 wt% PTFE solution) so that the amount of platinum becomes 4 mg / cm^2. Afterwards, by evaporating the solvent with vacuum drying the electrode sheets were obtained. The Nafion-117 was sandwiched between the two electrodes and then the assembly was subjected to hot-pressing at 150 °C under the pressure of 200 kgf / cm^2 for 60 seconds to make the assembly one body. The current collectors were applied to both surfaces of the body, and the inlets and the outlets of hydrogen and oxygen were set up to fabricate PEFC. Hydrogen and oxygen were fed to both compartments with 0.2 l / min at the ambient atmosphere. When the operating temperature was kept at 60 °C and the hydrogen gas was humidified, generation of electricity was confirmed over several hours under the condition of 0.4 V and 5 A.